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 CHRISTOS PAPANTONIOU



(54) COSMETIC COMPOSITIONS BASED ON COPOLYMERS PREPARED IN THE PRESENCE OF CERIUM IONS

(71) We, L'OREAL, a French Body Corporate, of 14, rue Royale, 75008 Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to cosmetic compositions.

These compositions are characterised in that they contain, in a suitable cosmetic vehicle, at least one copolymer obtained by copolymerising an unsaturated monomer with a compound having at least one OH group, the copolymerisation being carried out in an aqueous medium in the presence of cerium ions, the compositions being substantially free of cerium ions.

The compositions of the invention when applied in the form of wave-setting lotions or in the of lacquers, to the hair, produce an excellent hold of the hairstyle and render the hair soft and glossy.

Furthermore, it has been found that when these compositions are in the form of, for example, shampoos, rinses or dyeing compositions, they make it possible to render the hair easier to disentangle, to impart excellent gloss to the hair.

These compositions can also be in the form of milks, creams, lotions or foundations for application to the skin, for example, the face. The particular copolymers specified above impart excellent properties to such compositions, so that these copolymers can be used as a replacement for those usually employed in this type of composition.

Equally, these copolymers can advantageously replace the resins employed in compositions in the form of nail varnishes, making it possible to impart good adhesion, good lasting qualities and excellent gloss to the nail varnish.

According to the invention, the compound which has at least one OH group (or prepolymer) can be a natural, modified or unmodified compound, or a polymeric or non-polymeric synthetic compound.

Examples of such natural compounds include gelatine, cellulose, starch, modified starches, collagen, chitosans, nitrocellulose, cellulose ethers and cellulose carrying cationic groups.

Examples of such synthetic compounds include:

(i) polymers having a polymeric hydrocarbon chain such as polyvinyl alcohols, partially hydrolysed polyvinyl acetates, partially or completely hydrolysed N-vinylpyrrolidone/vinyl acetate copolymers, partially or completely hydrolysed crotonic acid/vinyl acetate copolymers, polyvinylpyrrolidone (di-OH), polyacrylamide (di-OH), poly(2 - N,N - dimethylamino - ethyl methacrylate) (di-OH) quaternised with ethyl bromide, polybutadienes with terminal OH groups such as those known under the tradenames of "HYCAR HTB" sold by GOODRICH ["Hycar" is a Registered Trade Mark], "NISSO PBG 2000" sold by NIPPON SODA, "R 15" sold by SINCLAIR KOPPERS, "BUTAREZ HT" sold by PHILLIPS PETROLEUM and "TELAGEN HT" sold by GENERAL TIRE, polyisobutylene with terminal OH groups such as that known under the tradename of "HTPIB" sold by ENJAY POLYMER, and copolymers of N-methacryloyl-D-glucosamine such as N-vinylpyrrolidone/N-methacryloyl-D-glucosamine (di-OH or not) copolymers, (the notation "(di-OH)" is used herein to indicate polymers having two terminal OH groups); and

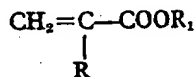
(ii) polymeric compounds having a hydrocarbon chain which contains hetero-

atoms, such as polyethylene glycol, polypropylene glycol, ethylene oxide/propylene oxide copolymers, ethylene oxide/polysiloxane copolymers and polyoxyethyleneated nonylphenols.

As a non-polymeric compound, pentaerythritol is particularly preferred.

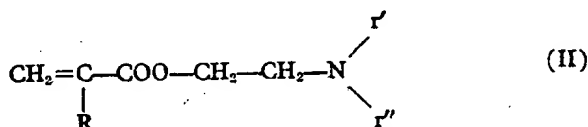
The unsaturated monomers which are copolymerised with the compound having at least one OH group can be of various types; examples of these include:

- a) acrylic acid or methacrylic acid;
- b) acrylic or methacrylic esters of the formula:



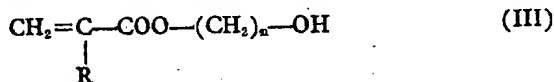
in which R represents a hydrogen atom or a methyl radical and R₁ represents a linear or branched alkyl radical of up to 18 carbon atoms, particular examples of these compounds being methyl, ethyl, propyl, tertiary butyl, octyl, dodecyl and octadecyl acrylate and methacrylate;

- c) N,N-dialkylaminoethyl acrylates or methacrylates of the formula:



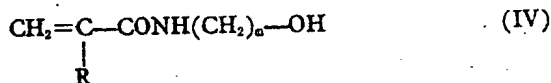
in which R is as defined above and each of r' and r'' represents an alkyl radical of 1 to 5 carbon atoms, particular examples of these compounds being 2-N,N-dimethyl-aminoethyl acrylate or methacrylate, and 2-N,N-diethylaminoethyl acrylate or methacrylate; or a corresponding quaternary ester;

- d) hydroxyalkyl acrylates or methacrylates of the formula:



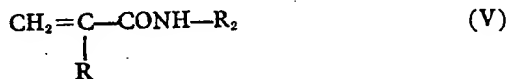
in which R is as defined above and n is 2 or 3, particular examples of these compounds being 2-hydroxyethyl acrylate and methacrylate and 3-hydroxypropylacrylate and methacrylate;

- e) acrylamide or methacrylamide;
- f) hydroxyalkylacrylamides of the formula:



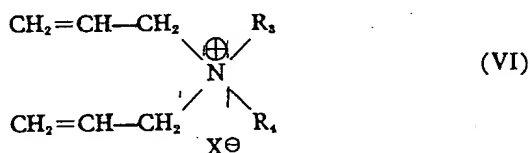
in which R is as defined above and n is 1, 2 or 3, particular examples of these compounds being hydroxyethylacrylamide and hydroxypropylacrylamide;

- g) N-alkylacrylamides and N-alkylmethacrylamides of the formula:



in which R is as defined above and R₂ represents a linear or branched alkyl radical of up to 5 carbon atoms, particular examples of these compounds being N-methylacrylamide and N-tertiary-butylacrylamide; and

- h) N,N-diallyl-N,N-dialkylammonium chlorides or bromides of the formula:



in which each of R_3 and R_4 represents a linear or branched alkyl radical of up to 16 carbon atoms and X is Cl or Br, particular examples of these compounds being N,N-diallyl - N - methyl - N - dodecylammonium chloride or bromide, N,N - diallyl - N - methyl - N - butylammonium chloride or bromide, N,N - diallyl - N - methyl - N - octylammonium chloride or bromide and N,N - diallyl - N - methyl - N - decylammonium chloride or bromide.

If the compound which has at least one OH group, (or prepolymer), is a homopolymer and possesses a single OH group at one of its ends, the polymerisation in the presence of an unsaturated monomer such as those enumerated above in that case leads to a block polymer and, more particularly, to a two-block polymer.

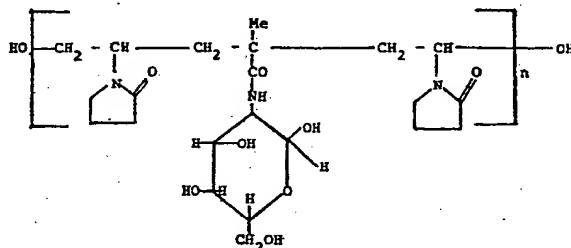
On the other hand, if the homopolymer possesses two OH groups, one at each of its ends, a three block polymer is obtained.

Thus, if the homopolymer which is employed is polyvinylpyrrolidone (di-OH), polymerisation with methyl methacrylate (MMA) gives a three-block polymer which can schematically be represented as follows:



If, on the other hand, the compound which has at least one OH group is a copolymer and possesses an OH group at least one of its ends and also possesses at least one lateral OH group, polymerisation in the presence of an unsaturated monomer leads to a copolymer which is both a block copolymer and a graft copolymer.

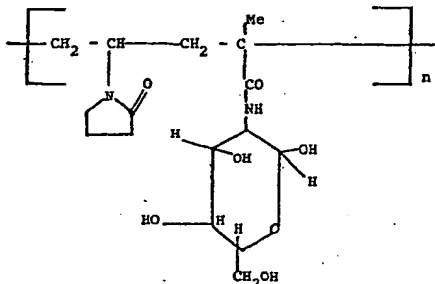
Thus, if a N - vinylpyrrolidone/N - methacryloyl - D - glucosamine (di-OH) copolymer of the formula given below is used as the compound having lateral and terminal OH groups,



and if this compound is copolymerised with, for example, methyl methacrylate, a compound is obtained which possesses, firstly, poly(methyl methacrylate) (PMMA) blocks at each of the ends of the polymer chain and, secondly PMMA grafts on each or some of the OH groups of the glucosamine molecules.

In another embodiment, the compound which has at least one OH group can be a copolymer which does not contain terminal OH groups but contains at least one lateral OH group, so that in the presence of an unsaturated monomer the polymerisation leads to a polymer which is merely grafted.

Thus, if a polymer of the following formula:



is used as the copolymer which has at least one lateral OH group and if this compound is copolymerised with methyl methacrylate, a copolymer is obtained which contains PMMA grafts on each or some of the OH groups of the glucosamine.

The compound which has at least one OH group can also be a non-polymeric

compound such as, for example, pentaerythritol, or another compound which carries four OH groups, and in that case polymerisation with an unsaturated monomer, such as, for example methyl methacrylate, leads to a compound containing grafts on each or some of the OH groups, these grafts being PMMA grafts; these copolymers are referred to herein as "star-shaped copolymers" i.e. a copolymer in which there are three or more separate polymeric chains radiating from a central monomeric unit.

It will be understood that it is difficult to give a range of molecular weights for these copolymers, firstly taking into account that the prepolymer may be of polymeric or non-polymeric dimensions and secondly taking into account the number of blocks or the degree of grafting. Hence, the molecular weights can vary greatly and essentially depend on the cosmetic use to which the copolymers are intended to be put.

The copolymers used according to the invention, whether they are block copolymers block and graft copolymers graft copolymers or star-shaped copolymers are prepared in accordance with a process which consists of reacting the compound which has at least one OH group, in aqueous solution, in the presence of an unsaturated monomer and of a cerium salt such as, for example, cerium ammonium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$.

Suitable conditions for this process, which are known (see L. J. GUILBAULT et al., J. Macro. Sci. Chem. A7(8), page 1,581 (1973)) are as follows:

The prepolymer and the monomer or monomers to be copolymerised, are introduced, in aqueous solution (distilled water), into a reactor equipped with a stirrer and a nitrogen inlet tube. A sufficient amount of ammonium cerium nitrate for forming the number of blocks and/or the degree of grafting desired is then introduced into this mixture.

It is obvious that for this reason the amount of catalyst can vary within very wide limits.

Preferably, the ammonium cerium nitrate is introduced as a solution in N nitric acid.

The mixture is then stirred for a period which can vary from 2 to 48 hours, either at ambient temperature or at a temperature of 40° to 80°C.

After the end of the polymerisation, the copolymer formed is precipitated by means of an organic solvent such as ether, isopropyl alcohol, acetonitrile, acetone or mixtures of such solvents. Since the cerium compound will not be precipitated, it is clear that the polymer is then substantially free of cerium.

It is important to note that for certain prepolymers their preparation must be carried out under special conditions, for example, in aqueous solution in the presence of H_2O_2 as an initiator and of a compound such as borax, in order to produce terminal OH groups on the polymeric chain. Such is the case, for example, with polyvinylpyrrolidone (di-OH) or polyacrylamide (di-OH), or an N - vinylpyrrolidone/N-methacryloyl - D - glucosamine (di-OH) copolymer.

It has not been possible to determine the exact structure of the copolymers in the compositions of the invention with certainty, because the radical formed by reduction of the Ce^{IV} to Ce^{III} in the presence of at least one OH group can be located either on the oxygen of the OH or on the adjacent carbon.

The cosmetic compositions according to the invention contain the polymers defined above either by way of the principal active ingredient or by way of an additive.

These cosmetic compositions can be in the form of aqueous, alcoholic or aqueous-alcoholic solutions, the alcohol being, in particular, a lower alkanol such as ethanol or isopropanol, or can be in the form of creams, gels, emulsions or milks, or in the form of aerosols in pressurised containers which contain a propellant, for example a mixture of at least one alcohol and a liquefied propellant gas under pressure, or in the form of nail varnishes.

The adjuvants generally present in the cosmetic compositions of the invention are, for example, perfumes, dyestuffs, colourants for dyeing the composition, anti-sunbeam agents, preservatives, sequestering agents and thickeners.

It should be noted that the cosmetic compositions according to the invention may be either ready-to-use compositions or concentrates which must be diluted before use. The cosmetic compositions of the invention are thus not limited to a particular range of polymer concentration.

In general, in the cosmetic compositions according to the invention, the copolymer concentration is 0.1 to 15% by weight, preferably 0.5 to 10%.

The cosmetic compositions based on the polymers described above in particular exhibit valuable cosmetic properties when they are applied to the hair.

Thus, when they are applied to the head of hair they significantly improve the

properties of the hair. For example, they assist the treatment and facilitate the disentangling of wetted hair.

These cosmetic compositions for hair generally contain at least one adjuvant usually employed in cosmetic compositions for hair.

5 These cosmetic compositions for hair can be in the form of aqueous, alcoholic or 5
aqueous-alcoholic solutions (the alcohol being, in particular, a lower alkanol such as
ethanol or isopropanol) or in the form of creams, gels or emulsions, or in the form
of sprays. They can also be packaged in the aerosol containers, and contain a propellant
10 such as, for example, nitrogen, nitrous oxide or chlorofluorinated hydrocarbons of the
"Freon" (Registered Trade Mark) type, such as Freon 11 and Freon 12 or mixtures 10
of these propellants.

The adjuvants usually present in the cosmetic compositions for hair according to the invention are, for example, perfumes, dyestuffs, preservatives, sequestering agents, thickeners and emulsifiers.

15 The copolymers can be present in the cosmetic compositions for hair, according to 15
the invention, either as an additive or as the main active ingredient, in wave-setting
lotions, treatment lotions, hair-styling creams or gels or as an additive in shampoos,
wave-setting lotions, permanent waving lotions, dyeing lotions, restructuring lotions,
treatment lotions or hair lacquers.

20 The cosmetic compositions for hair, according to the invention, are thus especially: 20
a) Treatment compositions which contain, by way of active ingredient, at least
one of the copolymers in aqueous or aqueous-alcoholic solution.

The copolymer content is suitably 0.1 to 10% by weight, preferably 0.1 to 5%.

25 The pH of these lotions is suitably near the neutral point, for example, from 25
6 to 8. It is possible, if necessary, to bring the pH to the desired value by adding
either an acid, such as citric acid, or a base, especially an alkanolamine such as mono-
ethanolamine or triethanolamine.

In order to treat the hair with such a lotion, the said lotion is suitably applied to the wetted hair and allowed to act for 3 to 15 minutes, after which the hair is rinsed.

30 Thereafter, if desired, a conventional wave-setting can be carried out. 30

b) Shampoos which contain at least one of the copolymers and a cationic, non-ionic or anionic detergent.

The cationic detergents are, in particular, long-chain quaternary ammonium compounds, esters of fatty acids and amino alcohols, or polyether-amines.

35 The non-ionic detergents are, in particular, esters of polyols and sugars, conden- 35
sation products of ethylene oxide with fatty compounds, with long-chain alkylphenols,
with long-chain mercaptans or with long-chain amides, and polyethers of polyhydroxylic
fatty alcohols.

40 The anionic detergents are especially the alkali metal salts, the ammonium salts 40
or the amine or aminoalcohol salts of fatty acids such as oleic acid, ricinoleic acid,
copra oil acids or hydrogenated copra oil acids; the alkali metal salts, the ammonium
salts or the aminoalcohol salts of sulphates of fatty alcohols, especially of C_{12} — C_{14}
fatty alcohols and C_{16} fatty alcohols; the alkali metal salts, the magnesium salts, the
45 ammonium salts or the aminoalcohol salts of the sulphates of oxyethylenated fatty 45
alcohols; the condensation products of fatty acids with, for example, isethionates,
taurine, methyltaurine, or sarcosine; the alkylbenzenesulphonates, especially with C_{12}
alkyl; the alkylaryl-polyether-sulphates and the monoglyceride sulphates. All these
anionic detergents, as well as numerous others not mentioned here, are well known
and are described in the literature.

50 These compositions in the form of shampoos can also contain various adjuvants 50
such as, for example, perfumes, dyestuffs, preservatives, thickeners, foam stabilisers,
softeners or other cosmetic resins.

In these shampoos, the detergent concentration is generally 5 to 50% by weight and the copolymer concentration is generally 0.1 to 10%, preferably 0.1 to 5%.

55 c) Wave-setting lotions, especially for sensitised hair, which contain at least one 55
of the copolymers in aqueous, alcoholic or aqueous-alcoholic solution.

These compositions can furthermore contain another cosmetic resin.

The concentration of copolymer in these wave-setting lotions is generally 0.1 to 5% by weight, preferably 0.2 to 3%.

60 The pH of these wave-setting lotions is generally 3 to 9, preferably 4.5 to 7.5 60
The pH can be altered, if desired, for example, by adding an alkanolamine such as
monoethanolamine or triethanolamine.

d) Hair dyeing compositions which contain at least one of the copolymers, a dyestuff and a carrier.

65 The carrier is preferably so chosen as to form a cream, a gel or an emulsion. 65

The copolymer concentration in these dyeing compositions is suitably 0.5 to 15% by weight, preferably 0.5 to 10%.

In the case of an oxidation dyeing, the dyeing composition can be packaged in two parts, the second part being hydrogen peroxide, and the two parts are mixed at the time of use.

e) Hair lacquers which contain an alcoholic or aqueous-alcoholic solution of at least one of the copolymers, this solution being placed in an aerosol container and mixed with a propellant.

For example, it is possible to obtain an aerosol lacquer according to the invention by adding the copolymer to a mixture of an anhydrous aliphatic alcohol such as ethanol or isopropanol and a liquefied propellant or a mixture of liquefied propellants such as the halogenated hydrocarbons trichlorofluoromethane or dichlorodifluoromethane or their mixtures.

In these hair lacquer compositions, the polymer concentration is generally 0.1 to 3% by weight.

Of course it is possible to add to these hair lacquers adjuvants such as dyestuffs, plasticisers or any other usual adjuvant.

The polymers according to the invention also exhibit valuable cosmetic properties when they are applied to the skin.

In particular, they favour the hydration of the skin, thus avoiding its drying out. They furthermore impart to the skin a significant softness to the touch.

The cosmetic compositions according to the invention can also be cosmetic compositions for application to the skin.

Furthermore they generally contain at least one adjuvant usually employed in cosmetic compositions for the skin.

The cosmetic compositions for the skin, according to the invention, may be, for example, in the form of creams, gels, emulsions or aqueous, alcoholic or aqueous-alcoholic solutions.

The copolymer concentration in these compositions for the skin is generally 0.1 to 10% by weight.

The adjuvants generally present in these cosmetic compositions are, for example, perfumes, dyestuffs, preservatives, thickeners, sequestering agents and emulsifiers.

These compositions for the skin in particular constitute creams or treatment lotions for the hands or the face, anti-sunburn creams, tinted creams and make-up remover milks.

These compositions may be prepared in accordance with the usual methods.

For example, in order to obtain a cream, an aqueous phase containing the copolymer and, optionally, other ingredients or adjuvants in solution, and an oily phase, can be emulsified together.

The oily phase can consist of various products such as paraffin oil, vaseline oil, sweet almond oil, avocado oil, olive oil, fatty acid esters, such as glyceryl monostearate, ethyl or isopropyl palmitate, or alkyl myristates such as propyl, butyl or cetyl myristate. It is furthermore possible to add fatty alcohols such as cetyl alcohol or waxes such as beeswax.

The compositions according to the invention can also be in the form of a nail varnish and preferably contain 3 to 15% by weight of the copolymer in association with a plasticiser, a film-forming agent and a solvent system, that is to say the usual solvents and/or conventional diluents for this type of composition, the solvent system preferably constituting from 60 to 80% by weight of the varnish.

In certain cases, these varnishes can also contain colourants in a proportion of 0.05% to 6% by weight based on the total weight of the varnish.

These varnishes according to the invention impart excellent gloss and have good keeping qualities.

Several Examples of the preparation of polymers, as well as Examples of cosmetic compositions according to the invention, will now be given by way of illustration.

PREPARATION EXAMPLES PREPARATION OF THE PREPOLYMERS EXAMPLE 1.

Preparation of a polyvinylpyrrolidone prepolymer containing one-OH group at each chain end.

100 g of freshly distilled N-vinylpyrrolidone, 500 g of distilled water and 1.5 g of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) are introduced into a 1 litre flask. The reaction mixture is heated to 40°C under a stream of nitrogen, whilst stirring.

After the borax has dissolved, 1 ml of 110 volumes strength H_2O_2 is introduced and the temperature is kept at $40^\circ C$ for 7 hours. The polymer is precipitated in acetone and dried under reduced pressure. 99 g of pure polymer are thus obtained.

Viscosity: 4.5 cpo (at $34.6^\circ C$, in 5% strength solution in water).

5

EXAMPLE 2.

5

Preparation of a N-vinylpyrrolidone/N-methacryloyl-D-glucosamine prepolymer. 100 g of ethanol, 95 g of distilled N-vinylpyrrolidone, 5 g of N-methacryloyl-D-glucosamine and 1 g of azo-bis-isobutyronitrile are introduced into a 500 ml flask equipped with a stirrer and a nitrogen inlet tube.

10

The mixture is heated at $80^\circ C$ for 16 hours and the polymer is then precipitated in acetone (yield, 60%).

10

Viscosity: 1.8 cpo (at $34.6^\circ C$, in 5% strength solution in water).

EXAMPLE 3.

15

Preparation of a partially hydrolysed prepolymer of N-vinylpyrrolidone and vinyl acetate.

15

800 ml of ethanol, 12.8 g of sodium hydroxide pellets and 80 g of a copolymer composed of 70% of N-vinylpyrrolidone and 30% of vinyl acetate are introduced into a 2 litre flask. The reaction mixture is kept at $30^\circ C$, whilst stirring, for 2 hours and is then poured into 8 litres of diethyl ether. After filtration, the polymer is dried under reduced pressure.

20

Yield: 95%.

20

EXAMPLE 4.

25

Preparation of a partially hydrolysed prepolymer of crotonic acid and vinyl acetate.

25

Following the same method of working as above, a copolymer composed of 90% of vinyl acetate and 10% of crotonic acid is hydrolysed in the presence of sodium hydroxide.

Yield 95%.

EXAMPLES 5 to 12.

30

The preparation of certain prepolymers obtained according to the method of working of either Example 1 or Example 2 has been set out in Table I.

30

TABLE I

Example No.	Monomers	Amount (g)	AIBN (a)	H ₂ O ₂ 110' strength (ml)	Borax (g)	Water (ml)	Ethanol	Reaction Temperature (°C)	Reaction time (hours)	Precipitant	Yield %	Viscosity (cPo) (d)
5	N-vinylpyrrolidone (di-OH)	100		5	2.5	100		40	7	acetone	99	1.9
6	N-vinylpyrrolidone (di-OH)	100		20	2	80		40	6	acetone	98	2.07
7	N-vinylpyrrolidone (di-OH)	1,000		50	10	1,000		40	7	acetone	90	1.42
8	N-vinylpyrrolidone (di-OH)	100		2	1	100		40	6	acetone	95	2.28
9	N-vinylpyrrolidone (di-OH)	100		10	4	500		40	24	acetone	80	3.95
10	2-N,N-dimethylaminoethyl methacrylate (di-OH) quaternised with ethyl bromide	100		10	4	500		40	24	ethanol	70	2.0
11	N-vinylpyrrolidone/ N-methacryloyl-D-glucosamine	90 10	1				100	80	16	acetone	70	1.85
12	N-vinylpyrrolidone/ N-methacryloyl-D-glucosamine (di-OH)	80 20	1			500		40	16	acetone	60	

(a) Azo-bis-isobutyronitrile

(b) Na₂B₄O₇·10H₂O

(c) The pH is kept above 9 during the polymerisation by adding supplementary amounts of Borax.

(d) In 5% strength solution in water at 34.6°C.

PREPARATION OF THE COPOLYMERS

All the starting materials used are purified.

PREPARATION OF THE CATALYST:

5 The cerium ammonium nitrate (CAN) solution is prepared by dissolving 58.5 g of cerium ammonium nitrate in a 1N nitric acid solution and making up to 1 litre with the same solution of nitric acid.

EXAMPLE 13.

Preparation of a poly(methyl methacrylate)/poly-N-vinylpyrrolidone/poly-(methyl methacrylate), (PMMA — PVP — PMMA), three-block copolymer.

1,250 ml of distilled water and 95 g of polyvinylpyrrolidone (di-OH) prepared according to Example 1 are introduced into a 2 litre flask equipped with a stirrer and a nitrogen inlet tube. 5 g of distilled methyl methacrylate and 50 ml of a cerium ammonium nitrate solution in nitric acid (CAN) are then introduced. The mixture is stirred for 4 hours at ambient temperature and is then poured into a mixture of ethyl ether and isopropanol. The mixture precipitated in this way is dissolved in dimethylformamide and reprecipitated from diethyl ether. Yield, 70%.

EXAMPLE 14.

Preparation of a block and graft copolymer of polyvinyl alcohol and 2-N,N-dimethylaminoethyl methacrylate (50/50) quaternised with dimethyl sulphate.

670 ml of water and 50 g of polyvinyl alcohol sold by Messrs. PROLABO [Registered Trade Mark] under the tradename of "Rhodoviol" [Registered Trade Mark] A/125P are introduced into a 2 litre flask equipped with a stirrer and a nitrogen inlet tube. The mixture is heated to 80°C, whilst stirring, until the polyvinyl alcohol has dissolved completely, and is then cooled to 20°C. 50 g of 2-N,N-dimethylaminoethyl methacrylate quaternised with dimethyl sulphate and 50 ml of a cerium ammonium nitrate solution in nitric acid (CAN) are then introduced.

The reaction mixture is stirred for 16 hours at ambient temperature and the polymer is then precipitated in a 3/2 mixture of acetone and isopropanol.

After filtration, the polymer is dried under reduced pressure.

Yield, 98%.

EXAMPLE 15.

Preparation of a block and graft copolymer of polyvinyl alcohol and N-vinylpyrrolidone (50/50).

Following the same method of working as that of Example 14, 50 g of distilled N-vinylpyrrolidone are polymerised onto 50 g of polyvinyl alcohol over the course of 16 hours. The polymer is precipitated in a 3/2 mixture of acetone and isopropanol.

EXAMPLE 16.

Preparation of a three-block copolymer by cyclopolymerisation of N,N-diallyl-N,N-dimethylammonium bromide onto poly-N-vinylpyrrolidone (di-OH).

500 ml of distilled water and 25 g of polyvinylpyrrolidone (di-OH) prepared according to Example 1 are introduced into a 500 ml flask equipped with a stirrer and a nitrogen inlet tube. 25 g of N,N-dimethyl-N,N-diallylammonium bromide and 25 ml of a solution of cerium ammonium nitrate in nitric acid (CAN) are then introduced. The mixture is stirred at 40°C for 48 hours and is then poured into acetonitrile. The polymer which has precipitated is dried under reduced pressure. 15 g of pure polymer are obtained. Yield 30%.

EXAMPLE 17.

Preparation of a three-block copolymer by cyclopolymerisation of N,N-diallyl-N-dodecyl-N-methylammonium bromide onto poly-N-vinylpyrrolidone (di-OH).

Using the method of Example 16, 25 g of N,N-diallyl-N-dodecyl-N-methylammonium bromide are polymerised onto 25 g of poly-N-vinylpyrrolidone (di-OH). 10 g of pure polymer are obtained by precipitation in acetonitrile. Yield 20%.

EXAMPLES 18 to 52.

The preparation of these copolymers is as set out in Table II.

TABLE II

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reaction Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
18	block	Prepolymer of Example 8 Methyl methacrylate	9 1	125	5	30	3 hrs. 30 mins.		acetonitrile
19	block	Prepolymer of Example 6 2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	5 5	125	5	30	24 hr.		ethyl ether
20	block	Prepolymer of Example 6 2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	9 1	125	5	30	24 hr.		ethyl ether
21	block	Prepolymer of Example 8 Acrylic acid	9 1	125	5	30	16 hrs.		1/1 mixture of ethyl ether and isopropanol
22	block	Prepolymer of Example 6 Acrylamide	5 5	125	5	30	16 hrs.		ethyl ether
23	block	Prepolymer of Example 8 Acrylamide	8 2	125	5	30	24 hrs.		1/1 mixture of ethyl ether and isopropanol

TABLE II (Continued)

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reaction Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
24	block	Prepolymer of Example 8 N,N-diallyl-N,N-dimethyl-ammonium bromide	150 150	2,700	150	40	48 hrs.	45	acetonitrile
25	block	Prepolymer of Example 7 Lauryl methacrylate	50 50	900	50	40	18 hrs.	75	acetone
26	block	Prepolymer of Example 9 2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	50 50	1,100	50	40	24 hrs.	90	acetone
27	block	Prepolymer of Example 10 Methyl methacrylate	9 1	125	5	30	4 hrs.		acetone
28	block	Prepolymer of Example 2 Methyl methacrylate	8 2	125	5	30	24 hrs.	80	acetone
29	block	Prepolymer of Example 11 Acrylamide	9 1	125	5	30	24 hrs.	85	acetone

TABLE II (Continued)

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reaction Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
30	block and graft	Prepolymer of Example 12	8	125	5	30	60 hrs.	80	acetone
		Methyl methacrylate	2						
31	block and graft	Polyvinyl alcohol (Rhodoviol 4/125 P)	20	670	50	25	16 hrs.	98	acetone/iso-propanol = 3/2
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	80						
32	block and graft	Polyvinyl alcohol (Rhodoviol 4/125 P)	20	670	50	25	16 hrs.	70	acetone/iso-propanol = 3/2
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	80						
33	block and graft	Polyvinyl alcohol (Rhodoviol 4/125 P)	15	200	12	25	4 hrs.	60	acetone
		Acrylamide	15						
34	block	Polyethylene glycol (molecular weight = 20,000)	50	900	50	30	48 hrs.	20	acetone
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	50						

TABLE II (Continued)

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reaction Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
35	star-shaped	Pentaerythritol	14	900	10	30	48 hrs.	45	acetone
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	80						
36	block and graft	Methylcellulose (Methocel A-15)	35	900	30	30	24 hrs.	40	heptane/iso-propanol
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	115						
37	block and graft	Methylhydroxypropylcellulose (Pharmacoat 603)	35	900	30	30	24 hrs.	40	heptane/iso-propanol
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	115						
38	block and graft	Hydroxyethylcellulose (Cellosize WP-09)	35	900	30	30	24 hrs.	40	heptane/iso-propanol
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	115						

TABLE II (Continued)

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reactant Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
39	block and graft	Methylhydroxybutylcellulose (Methocel HB)	35	900	30	30	24 hrs.	40	heptane/isopropanol
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	115						
40	block and graft	Methylhydroxypropylcellulose (Pharmacoat 603)	80	750	37.5	30	24 hrs.	40	ethyl ether/isopropanol
		Acrylamide	70						
41	block and graft	Methylcellulose (Methocel A-15)	80	1,150	37.5	30	24 hrs.	65	ethyl ether/isopropanol
		Acrylamide	70						
42	block and graft	Methylhydroxybutylcellulose (Methocel HB)	13	350	6.25	30	24 hrs.	20	ethyl ether/isopropanol
		Acrylamide	12						
43	block and graft	Carboxymethylcellulose (FinnFix 300)	80	750	37.5	30	24 hrs.	95	ethyl ether/isopropanol
		Acrylamide	70						

TABLE II (Continued)

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reaction Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
44	block and graft	Hydroxyethylcellulose	80	1,150	37.5	30	24 hrs.	90	ethyl ether/isopropanol
		Cellosize-WP-09							
45	block and graft	Acrylamide	70						
		Collagen (C-1633 type IV)	1						
46	block and graft	2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	1	10	0.5	30	24 hrs.	40	acetone
		Gelatine (ASF)	5						
47	block and graft	2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	5	125	5	40	24 hrs.	50	ethyl ether/isopropanol
		Prepolymer of Example 3	29	+25 ml EtOH					
47	block and graft	2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	30	450	30	30	24 hrs.	30	acetone/isopropanol

TABLE II (Continued)

Example No.	Form of Polymer Obtained	Nature of the Prepolymers and of the Monomers	Amount (g)	H ₂ O (ml)	CAN (ml)	Reaction Temperature (°C)	Reaction Time	Polymerisation Yield	Precipitant
48	block and graft	Prepolymer of Example 4	30	450	30	30	48 hrs.	35	ethyl ether/isopropanol
		2-N,N-dimethylaminoethyl methacrylate quaternised with ethyl bromide	30						
49	block and graft	Gelatine (ASF)	30	450	30	30	48 hrs.	35	acetone
		Methyl methacrylate	30						
50	block and graft	Methylhydroxybutylcellulose (Methocel-HB)	70	850	25	30	24 hrs.	30	acetone
		Hexyl methacrylate	30						
51	block and graft	Methylhydroxybutylcellulose (Methocel-HB)	9	350	6.25	30	48 hrs.	25	ethyl ether/isopropanol
		N-tertiary butylacrylamide	1						
52	block	Prepolymer of Example 4	9	125	5	30	48 hrs.	20	ethyl ether
		N-tertiary butylacrylamide	1						

EXAMPLES OF THE PREPARATION OF COMPOSITIONS

EXAMPLE A.

A wave-setting lotion is prepared in accordance with the invention by mixing the following ingredients:

5	Polymer prepared according to Example 13	2 g	5
	Perfume	0.1 g	
	Ethyl alcohol	50 g	
	Water q.s.p.	100 g	

10 This wave-setting lotion, applied in the conventional manner, makes it possible to impart to the hair a glossy appearance and excellent holding characteristics. 10

In this Example, the polymer prepared according to Example 13 can advantageously be replaced by the same amount of a polymer prepared according to Examples 14 to 16 and 25 to 30.

EXAMPLE B.

15 A wave-setting lotion is prepared in accordance with the invention by mixing the following ingredients: 15

	Polymer prepared according to Example 32	3.5 g	
	Perfume	0.1 g	
	Sufficient dyestuff to colour the lotion	0.2 g	
20	Isopropyl alcohol	50 g	20
	Water q.s.p.	100 g	

In this Example, the polymer prepared according to Example 32 can advantageously be replaced by the same amount of a polymer prepared according to Examples 15 and 33 to 43.

25 After impregnating the hair with one of the lotions according to this Example, the hair is wound up on wave-setting rollers having a diameter of 15 to 30 mm and is then dried by external application of heat. After removing the rollers, an excellent wave-set which holds very well is obtained. 25

EXAMPLE C.

30 A wave-setting lotion is prepared in accordance with the invention by mixing the following ingredients: 30

	Polymer prepared according to Example 28	3 g	
	Ethyl alcohol	50 g	
	Perfume	0.2 g	
35	Water q.s.p.	100 g	35

In this Example, the 3g of polymer according to Example 28 can advantageously be replaced by the same amount of one of the copolymers prepared according to Examples 16, 17 and 43 to 52.

EXAMPLE D.

40 An aerosol lacquer is prepared in accordance with the invention by mixing the following ingredients: 40

	Polymer prepared according to Example 13	8 g	
	Perfume	0.2 g	
	Absolute ethyl alcohol, q.s.p.	100 g	

45 25 g of this solution are then packaged in an aerosol container in the presence of 45 47 g of trichlorofluoromethane and 28 g of dichlorodifluoromethane.

After spraying, the hair is glossy, and soft to the touch and the resin is easily removed by brushing.

50 In this Example, the polymer according to Example 13 can advantageously be replaced by the same amount of a polymer prepared according to Examples 18, 22 and 23. 50

EXAMPLE E.

An aerosol lacquer is prepared in accordance with the invention by mixing the following ingredients:

	Polymer prepared according to Example 28	7.2 g	
	Perfume	0.3 g	
5	Isopropyl alcohol q.s.p.	100 g	5

25 g of this solution are then packaged in an aerosol container in the presence of 47 g of trichlorofluoromethane and 28 g of dichlorodifluoromethane.

After spraying, a hair lacquering which renders the hair glossy and soft to the touch is obtained.

10 In this Example, the polymer according to Example 13 can advantageously be replaced by the same amount of a polymer prepared according to Examples 22, 23 and 24. 10

EXAMPLE F.

15 A film-forming body milk is prepared, according to the invention, by mixing the following ingredients: 15

	Di-ethylhexyl adipate	4.8 g	
	Stearic acid	2.9 g	
	Lanolin alcohol ethoxylated with 5 mols of ethylene oxide	0.5 g	
20	Cetyl alcohol	0.4 g	20
	Glycerol stearate	1.0 g	
	Triethanolamine	0.95 g	
	Propylene glycol	4.8 g	
	Polymer prepared according to Example 14	0.5 g	
25	Preservative	q.s.	25
	Perfume	q.s.	
	Sterile demineralised water, q.s.p.	100 g	

In this Example, the polymer according to Example 14 can advantageously be replaced by the same amount of a polymer prepared according to Examples 15 to 20 and 33 to 43.

30 EXAMPLE G. 30

A film-forming cream is prepared according to the invention by mixing the following ingredients:

	Paraffin oil	30.0 g	
	Stearic acid	8.0 g	
35	Triethanolamine	1.0 g	35
	Polymer prepared according to Example 32	0.5 g	
	Preservative	q.s.	
	Perfume	q.s.	
	Sterile demineralised water, q.s.p.	100 g	

40 In this Example, the polymer according to Example 32 can advantageously be replaced by the same amount of a polymer prepared according to Examples 44 to 52 or Examples 13 to 20. 40

EXAMPLE H.

A skin lotion is prepared according to the invention by mixing the following ingredients:

45	Polymer prepared according to Example 32	1.0 g	45
	Propylene glycol	2.0 g	
	Ethanol	10.0 g	
	Methyl para-hydroxybenzoate (preservative)	0.2 g	
	Perfume	q.s.	
50	Dyestuff	q.s.	50
	Sterile demineralised water, q.s.p.	100 g	

The polymer is dissolved in the preservative solution (comprising the total amount of water+preservative) at 60°C.

After cooling, the other constituents are incorporated, with moderate stirring.

In this Example, the polymer according to Example 32 can be replaced by the same amount of a polymer prepared according to Examples 13, 18 to 24, 26 to 31 and 33 to 48.

EXAMPLE I.

A beauty mask is prepared, according to the invention, by mixing the following ingredients:

10	Polymer prepared according to Example 14	20.0 g	10
	Propylene glycol	5.0 g	
	Methyl para-hydroxybenzoate (preservative)	0.2 g	
	Ethanol	15.0 g	
	Kaolin	10.0 g	
15	Titanium oxide	0.5 g	15
	Triethanolamine lauryl-sulphate	6.0 g	
	Perfume	q.s.	
	Sterile demineralised water, q.s.p.	100 g	

The propylene glycol is dissolved in the preservative solution (comprising the total amount of water+preservative) at 60°C.

After cooling, the other constituents are incorporated, with moderate stirring.

In this Example, the polymer according to Example 14 can be replaced by the same amount of a polymer prepared according to Examples 15 to 20 and 44 to 52.

EXAMPLE J.

A foundation is prepared according to the invention by mixing the following ingredients:

	Partial glyceride of fatty acid	9.00 g	
	Cetyl/stearyl alcohol ethoxylated with 10 mols of ethylene oxide	4.00 g	
30	Paraffin oil	18.00 g	30
	Polymer prepared according to Example 14	1.00 g	
	Magnesium aluminium silicates	0.75 g	
	Rhodorsil anti-foaming agent	0.20 g	
	Alkyl para-hydroxybenzoates	0.20 g	
35	Water softened with an ion exchanger	66.85 g	35
	Inorganic colourants	5.00 g	
		<hr/> 105.00 g	

In this Example, the polymer according to Example 14 can be replaced by the same amount of a polymer prepared according to Examples 27 to 37 and 43 to 52.

EXAMPLE K.

A foundation is prepared according to the invention by mixing the following ingredients:

	Partial glyceride of fatty acid	9.00 g	
	Cetyl/stearyl alcohol ethoxylated with 10 mols of ethylene oxide	4.00 g	
45	Paraffin oil	18.00 g	45
	Polymer prepared according to Example 32	1.00 g	
	Magnesium aluminium silicates	0.75 g	
	Propyl para-hydroxybenzoate	0.20 g	
50	Water softened with an ion exchanger	66.85 g	50
	Inorganic colourants	5.00 g	
		<hr/> 105.00 g	

In this Example, the polymer according to Example 32 can be replaced by the same amount of a polymer prepared according to Examples 18 to 26 and 38 to 42.

EXAMPLE L.

A rinse in the form of a fluid emulsion is prepared, according to the invention, by mixing the following ingredients:

5	"Vaseline" (Registered Trade Mark) oil	9.5 g	5
	Polyglycerolated (2 to 6 mols) C_{16} — C_{18} fatty alcohols	6.5 g	
	Polymer obtained according to Example 18	1.5 g	
	Water q.s.p.	100 g	

10 This product is supplied to the washed and dried hair by distributing it carefully over the entire head of hair and massaging it gently. After an application time of about 2 minutes, the hair is carefully rinsed. The hair shows a brilliant sheen and is easy to disentangle. 10

In this Example, the polymer according to Example 18 can be replaced by the same amount of a polymer prepared according to Examples 28 to 35 and 38 to 43.

EXAMPLE M.

15 A rinse in the form of a gel is prepared, according to the invention, by mixing the following ingredients: 15

20	Hydroxyethylcellulose	0.9 g	
	Polymer obtained according to Example 36	0.8 g	
	Cetylpyridinium chloride	3 g	20
	Colourant	0.1 g	
	Water q.s.p.	100 g	

25 This product is applied to the washed and dried hair with gentle massaging. After an application time of 1 to 2 minutes, the head of hair is rinsed carefully. The hair is glossy and disentangles easily. 25

In this Example, the polymer according to Example 36 can advantageously be replaced by the same amount of a polymer according to Examples 45 to 52.

EXAMPLE N.

30 An anionic shampoo is prepared, according to the invention, by mixing the following ingredients: 30

35	Triethanolamine lauryl/myristyl-sulphate	12 g	30
	Copra diethanolamide	2 g	
	Myristyldimethylamine oxide	1.5 g	
	Polymer obtained according to Example 20	1.5 g	
	Lactic acid q.s.p.	pH=6.5	
	Water q.s.p.	100 g	35

40 This shampoo has excellent cosmetic properties. After it has been applied, the wetted hair is very easy to disentangle and after drying the hair is glossy, soft and supple. 40

In this Example, the same amount of the polymer according to Example 20 can advantageously be replaced by a polymer obtained according to Examples 21, 22, 24, 30, 41, 43 and 44.

EXAMPLE O.

45 A cationic shampoo is prepared, according to the invention, by mixing the following ingredients: 45

50	Cetyltrimethylammonium bromide	2 g	45
	Lauryl alcohol polyglycerolated with 4 mols of glycerol	12 g	
	Polymer obtained according to Example 16	1 g	
	Perfume	0.2 g	
	Lactic acid q.s.p.	pH=4.5	
	Water q.s.p.	100 ml	50

This shampoo, applied to the head of hair, produces a soft and frothy foam. It allows the wetted hair to be disentangled very easily. After drying, the hair is soft, very gloss and has a light appearance.

In this Example, the polymer according to Example 16 can advantageously be replaced by the same amount of a polymer prepared according to Examples 21 to 25 and 22 to 36.

EXAMPLE P.

5 A non-ionic shampoo is prepared according to the invention by mixing the following ingredients: 5

	C_{11} — C_{14} diol polyglycerolated with 3—4 mols of glycerol	17 g	
	Polymer obtained according to Example 40	2 g	
	Cetylpyridinium chloride	0.8 g	
10	Lauroyl diethanolamine	2.5 g	10
	Perfume	0.2 g	
	Lactic acid q.s.p.	pH=5.5	
	Water q.s.p.	100 ml	

15 This shampoo is limpid and produces a copious and rather soft foam.

It assists the disentangling of the wetted hair, whether it is natural, dyed or bleached. 15

After drying, the hair is soft, light and glossy.

In this Example, the polymer according to Example 40 can be replaced by the same amount of a polymer obtained according to Examples 41, 43 and 44.

20 EXAMPLE Q. 20

A dyeing composition, in the form of a gelled liquid, is prepared according to the invention.

	DYEING CARRIER		
	Oleyl alcohol glycerolated with 2 mols of glycerol	20 g	
25	Oleyl alcohol glycerolated with 4 mols of glycerol	20 g	25
	Butylglycol	8 g	
	Propylene glycol	12 g	
	Ammonia, 22° Bé strength	10 ml	
	Para-aminophenol base	0.08 g	
30	Meta-diaminoanisole sulphate	0.025 g	30
	Resorcinol	0.3 g	
	Meta-aminophenol base	0.06 g	
	Nitro-para-phenylenediamine	0.003 g	
	Para-toluylenediamine	1.05 g	
35	Hydroquinone	0.17 g	35
	Ethylenediaminetetraacetic acid	3 g	
	Sodium bisulphite, d=1.32	0.8 g	
	Water q.s.p.	100 g	

40 At the time of use, 5 g of a 35% strength solution of the polymer obtained according to Example 29 and 50 g of hydrogen peroxide of 20 volumes strength are admixed to 50 g of the carrier thus obtained. 40

This composition, thus obtained, is then applied to the hair by means of a paint-brush.

45 The composition is left in contact with the hair for 30 minutes and the hair is then rinsed. 45

Disentangling is easy and the hair is silky to the touch, glossy and bulky.

On deep chestnut hair, a light chestnut colour is obtained.

50 In this Example, the polymer according to Example 29 can advantageously be replaced by an equivalent amount of a polymer prepared according to Examples 16, 19 to 21, 23, 24, 26 and 35. 50

EXAMPLE R.

A nail varnish is prepared according to the invention by mixing the following ingredients:

	Nitrocellulose RS, $\frac{1}{2}$ second	16 g	
	Polymer obtained according to Example 50	6 g	
	Ethyl alcohol	4 g	
	Butyl alcohol	4 g	
5	Camphor	2 g	5
	Butyl phthalate	4 g	
	Toluene	20 g	
	Ethyl acetate	10 g	
	Butyl acetate	34 g	
10		<hr/> 100 g	10

This base varnish, applied to the nails, exhibits very good adhesion and excellent gloss which lasts well.

In this Example, the polymer according to Example 50 can without disadvantage be replaced by one of the polymers obtained according to Examples 40 to 44, 49 and 51.

EXAMPLE S.

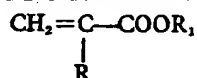
A coloured nail varnish is prepared according to the invention by mixing the following ingredients:

20	Base varnish as described in Example R	96.88 g	20
	Bentone 27 (benzylododecyldimethylammonium-montmorillonite)	1 g	
	Phosphoric acid	0.02 g	
	Titanium oxide	1 g	
25	D and C Red No. 7	0.4 g	25
	D and C Red No. 11	0.2 g	
	D and C Red No. 5	0.3 g	
	Red iron oxide	0.2 g	
		<hr/> 100 g	

This nail varnish exhibits excellent gloss and very good adhesion.

WHAT WE CLAIM IS:—

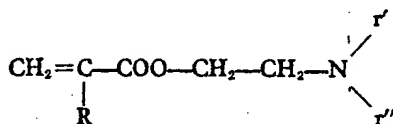
1. A cosmetic composition containing in a cosmetic vehicle, at least one copolymer obtained by copolymerising an unsaturated monomer with a compound which has at least one OH group, in an aqueous medium and in the presence of cerium ions, the composition being substantially free of cerium ions.
2. A composition according to claim 1 in which the cerium ions are derived from cerium ammonium nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.
3. A composition according to claim 1 or 2, in which the compound which has at least one OH group is gelatine, cellulose, starch, a modified starch, collagen, a chitosan, nitrocellulose, a cellulose ether or cellulose carrying cationic groups.
4. A composition according to claim 1 or 2 in which the compound which has at least one OH group is a polyvinyl alcohol, a partially hydrolysed polyvinyl acetate, a partially or completely hydrolysed copolymer of N-vinylpyrrolidone and vinyl acetate, a partially or completely hydrolysed copolymer of crotonic acid and vinyl acetate, a polyvinylpyrrolidone (di-OH), a polyacrylamide (di-OH), a poly(2-N,N-dimethyl-aminoethyl methacrylate) (di-OH) quaternised with ethyl bromide, a polybutadiene with terminal OH groups, a polyisobutylene with terminal OH groups or a copolymer of N-vinylpyrrolidone and N-methacryloyl-D-glucosamine (di-OH or not).
5. A composition according to claim 1 or 2, in which the compound which has one OH group is a polyethylene glycol, a polypropylene glycol, an ethylene oxide/propylene oxide copolymer, an ethylene oxide/polysiloxane copolymer or a poly-oxyethyleneated nonylphenol.
6. A composition according to claim 1 or 2, in which the compound which has at least one OH group is pentaerythritol.
7. A composition according to any one of the preceding claims in which the unsaturated monomer is:
 - (a) acrylic or methacrylic acid;
 - (b) an acrylic or methacrylic ester of the formula:



in which R represents a hydrogen atom or a methyl radical and R₁ represents a linear or branched alkyl radical of up to 18 carbon atoms;

(c) an N,N-dialkylaminoethyl acrylate or methacrylate of the formula:

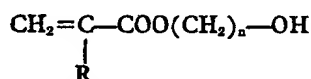
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5

in which R is as defined above and each of r' and r'' represents an alkyl radical of 1 to 5 carbon atoms; or a corresponding quaternary ester;

(d) a hydroxyalkyl acrylate or methacrylate of the formula:

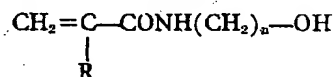


10 in which R is as defined above and n is 2 or 3;

10

(e) acrylamide or methacrylamide;

(f) a hydroxyalkylacrylamide of formula:

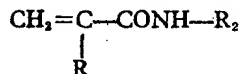


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in which R is as defined above and n is 1, 2 or 3;

(g) an N-alkylacrylamide or N-alkylmethacrylamide of the formula:

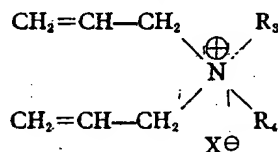
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in which R is as defined above and R₂ represents a linear or branched alkyl radical of up to 5 carbon atoms; or

(h) an N,N-diallyl-N,N-dialkylammonium chloride or bromide of the formula:

20



20

in which each of R₃ and R₄ represents a linear or branched alkyl radical of up to 16 carbon atoms and X is Cl or Br.

8. A composition according to any one of the preceding claims, in which the copolymer is a block copolymer.

25

9. A composition according to any one of claims 1 to 7, in which the copolymer is a block and graft copolymer.

25

10. A composition according to any one of claims 1 to 7, in which the copolymer is a graft copolymer.

30

11. A composition according to any one of claims 1 to 7, in which the copolymer is a star-shaped copolymer (as hereinbefore defined).

30

12. A composition according to any one of the preceding claims, which contains 0.1 to 15% by weight of the copolymer.

13. A composition according to claim 12 which contains 0.5 to 10% by weight of the copolymer.

35

14. A composition according to any one of the preceding claims in which the cosmetic vehicle is an aqueous, alcoholic, or aqueous-alcoholic solution, a cream, a gel, a milk or an emulsion.

35

15. A composition according to any one of claims 1 to 13, in which the cosmetic vehicle is a mixture of at least one alcohol and a liquefied propellant gas under pressure.

5 16. A composition according to claim 14 or 15, in which the alcohol is ethanol or isopropanol. 5

17. A composition according to any one of claims 1 to 14, in the form of a shampoo containing 5 to 50%, based on the weight of the composition, of a cationic, non-ionic or anionic detergent.

10 18. A composition according to any one of claims 1 to 14, suitable for dyeing hair, which contains a dyestuff in a carrier and is in the form of a cream, a gel or an emulsion. 10

19. A composition according to any one of claims 1 to 13 suitable for application to the skin, in which the cosmetic vehicle is a cream, a gel, an emulsion or a milk and which contains 0.1 to 10% by weight of the copolymer.

15 20. A composition according to any one of the preceding claims which contains a preservative, perfume, colourant for dyeing the composition, sequestering agent, thickener, emulsifier or anti-sunburn agent. 15

20 21. A composition according to any one of claims 1 to 13, in the form of a nail varnish containing a plasticiser, a film-forming agent, 3 to 15% by weight of the copolymer, and 60 to 80% by weight of a solvent system, the weight percentages being based on the weight of the composition. 20

22. A composition according to claim 21 containing 0.05% to 6%, based on the weight of the composition, of a colourant.

25 23. A composition according to claim 1 substantially as described in any one of Examples A to S. 25

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